Devolatilization Studies on Coal Vitrinoids
By Use of a Thermobalance

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The petrographic entities, which originate from the vegetation making up coal, help to establish the properties of coal that influence its mining, preparation, and use. Consequently, the properties of these entities should be known if the potential use of petrographic techniques and of the coal itself is to be made. Various physical and chemical properties of coals have been determined with significant contributions to the basic knowledge of coal and with practical application in industry, particularly in the carbonization of coal. To further exploit these entities, a study was initiated to determine their pyrolytic and plastic properties. In the initial phase, the vitrinoids of different rank coals were chosen for this study since vitrinoids are the most abundant and easiest entity to obtain from coal.

The thermal-decomposition behavior of entities has been visually examined in the hot-stage microscope. These observations are mostly qualitative. To obtain more quantitative results, the authors used a thermogravimetric balance (thermobalance) to determine the pyrolytic properties of the vitrinoids. The thermobalance, which has been used satisfactorily by numerous investigators,[1,2,3,4]* was selected because it continuously records the weight and temperature of the sample in respect to time as the sample is heated automatically.

When coal is heated, it not only devolatilized but also becomes fluid. Consequently, the plastic properties of coal have been associated with its pyrolytic properties. By using the rate of devolatilization and plastic properties, Soth and Russell[5] explained the coking pressure developed by coal blends. Van Krevelin,[3,6] Berkowitz,[7] and Brown[8] used the pyrolytic and plastic properties to present concepts of coal structure and the mechanism of carbonization. The relative plastic properties of the vitrinoids were obtained when possible, to determine the relationships that exist with their pyrolytic properties.

This paper presents the results of the thermogravimetric study on vitrinoids of various rank coals and the relationships of these results to the rank and plastic properties of the vitrinoids.

Materials and Experimental Work

The samples, high in vitrinoids, were selected from coking coals representing different ranks of coal. Because vitrinoids can be distinguished from the other coal entities by their bright luster in banded coals, these bright bands were removed with a table saw. The samples were then selected from these specimens with a dissecting needle under a magnifying glass. These samples, listed in Table I,

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* See References

were then pulverized to 100 percent minus 60 mesh. The volatile-matter content of these samples, determined by standard procedures (ASTM Test Designation D 271-58), are included in Table I. The petrographic analyses conducted by the procedures used at the U. S. Steel Corporation's Applied Research Laboratory (ARL)[9] are shown in Table II. These analyses indicate that the samples contained high concentrations of vitrinoids. Only Wellington and Donegan coal samples contained less than 90 percent vitrinoids, but even they contained more than 83 percent. The average reflectances were also determined on these samples, Table I.

The devolatilization measured by the weight loss was determined on a Stanton thermogravimetric balance, Model TR-1. This thermobalance continuously records the temperature and the weight of the samples that were automatically heated at a rate of 6 degress C per minute. The 0.5-gram sample was contained in a silica crucible supported by a silica weighing mechanism attached to the balance and heated by a tube furnace. The balance is sensitive to 1 milligram.

The plastic properties were determined in the Gieseler Plastometer by the standard procedures used in ASTM Test Designation D 1812-60T. The results of these tests are listed in Table III. The amount of sample was limited and, therefore, only single tests were made. Furthermore, the stirrer broke loose on some of the low-rank coals and no values could be obtained.

Results and Discussion

The data obtained from the thermobalance show the cumulative weight losses at corresponding temperatures. These "S"-type curves are presented in Figure 1. The initial level of weight loss reflects the total moisture content and amount of occluded gas in each sample, the low-rank coals containing high percentages of inherent moisture. In all samples the weight loss increased slightly for a short time after the first devolatilization; the temperature of the initial devolatilization increased with the rank of vitrinoids. Very rapid devolatilization then occurred for a considerable time (about 100 minutes) until the weight loss gradually decreased. Most of the volatile matter was driven off by the time the temperature reached 900 C.

To obtain additional information, the differential pyrolysis curves were then determined from these data. The graphs that show the rate of devolatilization with respect to temperature are shown in Figure 2. The maximum rates of devolatilization for the low-volatile coals are lower than those for the high-volatile coals. A summary of the maximum rate of devolatilization and the temperature of this maximum rate is listed in Table IV. The relationship between the maximum rate of devolatilization and volatile matter is shown in Figure 3. This relationship appears to substantiate published results which show that maximum devolatilization rates are obtained with coal containing about 35 percent volatile-matter content.[3] High-rank coals have much less volatile matter and, therefore, would be expected to have low rates of maximum devolatilization. However, since the low-rank high-volatile coals decompose at the lower temperatures because of their aliphatic structure, the devolatilization is distributed over a longer initial time or temperature range; therefore, the maximum rate would decrease after a certain rank coal was reached.

The results also indicate that the temperature of maximum rate of devolatilization increased as the rank of the coal increased. A good correlation is shown in Figure 4 where average reflectance is used as a rank parameter. A similar correlation is shown in Figure 5 where volatile matter is used.

Because plastic properties are related to rank, the temperature of maximum fluidity was related to the temperature of maximum rate of devolatilization. This relationship, shown in Figure 6, indicated a difference of about 50 degrees C between

these values. Published work on whole coals indicates that these values should be about the same.[3,6,7] However, the data reported by van Krevelen[3] show that the difference of 5 degrees per minute in the heating rate would account for about 20 degrees in the temperature of the maximum rate, since the faster the heating rate the higher the temperature.

The plastic properties and thermogravimetric analyses indicate that the vitrinoids start to decompose before they soften. However, the rapid devolatilization occurs at temperatures higher than the softening point for coal. In these vitrinoid samples, the maximum fluidity as measured in the Gieseler Plastometer occurred before the maximum rate of devolatilization. The relationships found in this study indicate that the thermal-decomposition characteristics can be estimated from the rank and plastic properties of the coal.

Summary

The results of this study indicated that the vitrinoids started to decompose before they became fluid. The initial temperature of devolatilization increased as the rank of the sample increased. Rapid devolatilization then occurred after the coal softened. From the differential pyrolysis curves, a good correlation was obtained between the temperature of maximum rate of devolatilization and the rank of coal. The maximum rate appears to be greatest for coals containing volatile matter (dry basis) of about 35 percent. The maximum fluidity of the vitrinoids was reached shortly before the temperature of maximum-rate devolatilization, and a good relationship was found between the temperature of maximum fluidity and the temperature of maximum rate of devolatilization.

The relationships obtained in this study indicate that the pyrolytic properties of coal can be estimated from its rank and plastic properties. This information should be useful to show what changes occur to coal when heated in the various processes used in industry.

References

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Table I

Identification and Rank of Vitrinoids

Rank of Original Coal	Seam	County	State	Concentration of Vitrinoids, %	Rank	
					Volatile Matter, % (dry basis)	Average Reflectance, R_o
High-Volatile B	Illinois No. 6	Vermilion	Illinois	97.3	43.7	0.50
High-Volatile C	Herrin No. 6	Saline	Illinois	95.3	38.3	0.51
High-Volatile B	Sunnyside	Carbon	Utah - Colorado	86.2	37.4	0.71
High-Volatile B	Herrin No. 6	Saline	Illinois	94.6	34.1	0.77
High-Volatile A	High Splint	Harlan	Kentucky	91.2	33.6	0.93
Medium-Volatile	Sewell	Nicolas	West Virginia	83.8	29.4	1.15
Medium-Volatile	"A"	Pitkin	Colorado	94.8	22.6	1.39
Low-Volatile	Pocahontas No. 3	McDowell	West Virginia	90.4	21.5	1.39
Low-Volatile	"A"	Pitkin	Colorado	97.0	16.5	1.42

Table II

Petrographic Entity Composition of Indicated Samples,* Volume Percent**

Coal	V4	V5	V6	V7	V8	V9	V10	V11	V12	V13	V14	V15	E	R	SF	Total
Illinois No. 6	49.6	45.7	2.0										0.9	-	0.1	98.3
Herrin No. 6 "C"	40.0	55.3											0.5	-	0.2	96.0
Sunnyside			35.3	50.0	0.9								1.0	8.8	0.2	96.2
Herrin No. 6 "B"			6.6	60.6	27.4								1.6	-	0.2	96.4
High-Splint				2.7	21.0	62.9	4.6						1.2	0.5	0.2	93.1
Sewell						2.5	12.6	46.1	20.9	1.7			3.5	0.2	0.6	88.1
Colorado Medium										61.6	33.2		-	-	0.3	95.1
Pocahontas No. 3										62.4	28.0		-	-	0.2	90.6
Colorado Low										34.0	61.1	1.9	-	-	0.1	97.1

(Columns V11–V15 are grouped under the heading "Reactive.")

Coal	SF	M	F	Total
Illinois No. 6	0.2	1.2	0.3	1.7
Herrin No. 6 "C"	0.5	3.0	0.5	4.0
Sunnyside	0.5	1.7	1.6	3.8
Herrin No. 6 "B"	0.4	2.5	0.7	3.6
High-Splint	0.4	5.7	0.8	6.9
Sewell	1.2	7.8	2.9	11.9
Colorado Medium	1.0	2.8	1.1	4.9
Pocahontas No. 3	0.9	7.2	1.3	9.4
Colorado Low	0.6	1.4	0.9	2.9

*Abbreviations for entities:
V4 = vitrinoid type 4, etc.
E = exinoids
R = resinoids
SF = semifusinoids
M = micrinoids
F = fusinoids

**Pure-coal basis (excluding mineral matter).
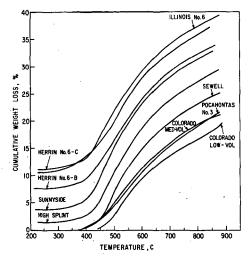
Table III

Plastic Properties of Vitrinoids*

| Sample | Maximum Fluidity | | Temperature Range, C | |
	ddpm** at	C	Softening	Solidification
Sunnyside	1.3	412	373	451
High-Splint	100	433	355	472
Sewell	16,300	443	385	485
Colorado Medium-Volatile	330	459	390	498
Pocahontas No. 3	432	466	397	499
Colorado Low-Volatile	80	467	401	503

*Stirrer broke loose on all Illinois coals.
**Dial divisions per minute.

Table IV

Summary of Thermogravimetric Analyses

Sample	Maximum Weight Rate Loss, % per minute	Temperature of Maximum Weight Rate Loss, C
Illinois No. 6	0.54	463
Herrin No. 6 "C"	0.47	480
Sunnyside	0.67	475
Herrin No. 6 "B"	0.48	490
High-Splint	0.60	483
Sewell	0.64	510
Colorado Medium-Volatile	0.40	520
Pocahontas No. 3	0.40	520
Colorado Low-Volatile	0.37	530

DEVOLATILIZATION OF VITRINOIDS

Figure 1

DIFFERENTIAL PYROLYSES CURVES OF VITRINOIDS

Figure 2

VOLATILE MATTER (DRY BASIS), %
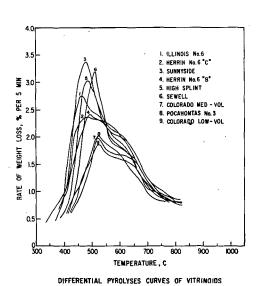
RELATIONSHIP OF VOLATILE MATTER AND
MAXIMUM RATE OF DEVOLATILIZATION

Figure 3

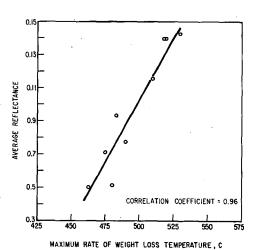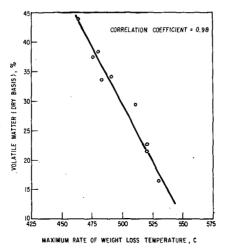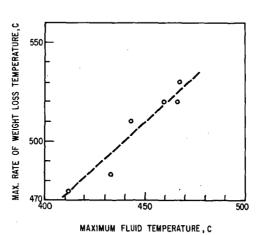MAXIMUM RATE OF WEIGHT LOSS TEMPERATURE, C

RELATIONSHIP OF THE TEMPERATURE OF MAXIMUM RATE
OF DEVOLATILIZATION AND RANK

Figure 4

RELATIONSHIP OF THE TEMPERATURE OF MAXIMUM RATE
OF DEVOLATILIZATION AND RANK

Figure 5

RELATIONSHIP OF MAXIMUM FLUIDITY AND
MAXIMUM RATE LOSS TEMPERATURES

Figure 6